(12)

OFFICE OF NAVAL RESEARCH

Contract N00014-81-K-0605

Task No. NR 056-768

TECHNICAL REPORT NO. 16

Selective Reactive Ion Etching of Tungsten Films in Fluorinated Gases

by

W-S. Pan and A. J. Steckl

Prepared for Publication in

Journal of Vacuum Science and Technology

Rensselaer Polytechnic Institute
Center for Integrated Electronics
Troy, NY 12181

July 1987

ADA183863

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION **unclassified**	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT **Approved for public release; distribution unlimited**
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) **RPI/CIE/TR-** 16	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION **Center for Integrated Electronics Rensselaer Polytechnic Institute**	6b. OFFICE SYMBOL (If applicable)
6c. ADDRESS (City, State, and ZIP Code) **Troy, NY 12181**	7a. NAME OF MONITORING ORGANIZATION **Office of Naval Research**
	7b. ADDRESS (City, State, and ZIP Code) **Chemistry Program Arlington, Virginia 22217**
8a. NAME OF FUNDING/SPONSORING ORGANIZATION **Office of Naval Research**	8b. OFFICE SYMBOL (If applicable)
8c. ADDRESS (City, State, and ZIP Code) **Chemistry Program Arlington, Virginia 22217**	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER **Contract N 00014-81-K-0605**
	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. **NR056-768** / PROJECT NO / TASK NO. / WORK UNIT ACCESSION NO

11. TITLE (Include Security Classification)

Selective Reactive Ion Etching of Tungsten Films in Fluorinated Gases

12. PERSONAL AUTHOR(S)

Wen-Sen Pan and Andrew J. Steckl

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Interim Technical	FROM _____ TO _____	July 1987	

16. SUPPLEMENTARY NOTATION

Prepared for publication in Journal of Vacuum Science and Technology

17. COSATI CODES		
FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)

Tungsten films, selectivity,
Reactive ion etching, fluorinated gases

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The use of reactive ion etching (RIE) with fluorinated gas plasmas, such as SF_6, CHF_3 and and CF_4 mixed with oxygen, to achieve selective patterning of tungsten films is reported. Rapid thermal annealing (RTA) was used to improve the properties of sputtered films. The resistivity of W films was found to decrease rapidly with annealing time (within 10sec) and to exhibit an Arrhenius behaviour with annealing temperature. The etch rates of W, Si and SiO_2 were measured as a function of oxygen percentage in the fluorinated gas plasma. The results on optimum selectivity indicate that a CHF_3/70%0 mixture results in W:Si and W:SiO_2 etch rate ratios of 2.4:1 and 2.1:1 for unannealed W films, and 1.6:1 and 1.8:1 for annealed samples, respectively. A higher W etch rate selectivity over SiO_2 was obtained in an SF_6/ 5% O_2plasma where the etch rate ratio is 11.6:1 for unannealed W films and 3:1 for annealed W samples. For reverse selectivity, the optimum W:SiO_2 etch rate ratios measured are 1:7.7 in pure CHF_3 gas

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS	**unclassified**
22a. NAME OF RESPONSIBLE INDIVIDUAL **Dr. David L. Nelson**	22b. TELEPHONE (Include Area Code) **(202)696-4410** / 22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR — 83 APR edition may be used until exhausted. All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

unclassified

for unannealed W and 1:4.6 for annealed W. The optimum W:Si reverse selectivity of 1:10 is obtained with an SF_6 /30%O_2 mixture plasma for both annealed and unannealed films. Satisfactory anisotropic edge profiles were obtained with CHF_3 /70%O_2 and SF_6 /5%O_2 where vertical-to-lateral etch ratios of 3.5:1 and 2:1 were measured.

(keywords :

SELECTIVE REACTIVE ION ETCHING OF TUNGSTEN FILMS IN FLUORINATED GASES

W-S. Pan and A.J. Steckl

Rensselaer Polytechnic Institute

Center for Integrated Electronics

Troy, N.Y. 12181

CONTENTS

Abstract

The use of reactive ion etching (RIE) with fluorinated gas plasmas, such as SF_6 , CHF_3 and CF_4 mixed with oxygen, to achieve selective patterning of tungsten films is reported. Rapid thermal annealing (RTA) was used to improve the properties of sputtered films. The resistivity of W films was found to decrease rapidly with annealing time (within 10sec) and to exhibit an Arrhenius behaviour with annealing temperature. The etch rates of W, Si and SiO_2 were measured as a function of oxygen percentage in the fluorinated gas plasma. The results on optimum selectivity indicate that a CHF_3/70%O mixture results in W:Si and W:SiO_2 etch rate ratios of 2.4:1 and 2.1:1 for unannealed W films, and 1.6:1 and 1.8:1 for annealed samples ,respectively. A higher W etch rate selectivity over SiO_2 was obtained in an SF_6/ 5% O_2 plasma where the etch rate ratio is 11.6:1 for unannealed W films and 3:1 for annealed W samples. For reverse selectivity, the optimum W:SiO_2 etch rate ratios measured are 1:7.7 in pure CHF_3 gas for unannealed W and 1:4.6 for annealed W. The optimum W:Si reverse selectivity of 1:10 is obtained with an SF_6/30%O_2 mixture plasma for both annealed and unannealed films. Satisfactory anisotropic edge profiles were obtained with CHF_3/70%O_2 and SF_6/5%O_2 where vertical-to-lateral etch ratios of 3.5:1 and 2:1 were measured.

I. Introduction

Refractory metals such as W or Mo are being increasingly

used in VLSI circuits for contact vias, gate and interconnect materials due to their high conductivity and thermal resistance [1,2,3,]. Recently,there has been considerable interest in W metallization because of its selective deposition properties [2,3,4,5]. The selective deposition of W from WF_6 gas involves reduction of the gas in the presence of Si and the formation of a W deposit and volatile SiF_4. While this is very useful for contact metallization, certain aspects of W interconnection technology still need to be explored. Since interconnections need to be deposited and patterned over various underlying materials with a minimum disturbance of the existing structure, we have investigated sputter-deposited W films, annealed by rapid thermal processing and patterned by reactive ion etching. The sputtering technique has the advantages of being essentially substrate-independent, taking place at room temperature and being able to cover large areas fairly easily. The RTA technique, with its very short operating time and high power density,was used to reduce the W resistivity while preventing such effects as oxidation of the W film , reaction between W and Si or SiO_2, and dopant redistribution[6]. Reactive ion etching was chosen because of the need for anisotropic fine line patterning.

The main objective of this work, therefore, was to investigate the conditions under which the anisotropic patterning of W films could be performed selectively with respect to Si and SiO_2. Since there are occasions during the fabrication process where the reverse selectivity is also highly desirable, in other

words, a W etch rate which is lower than that of other materials present ,especially SiO_2 and Si, this was investigated as well. The fluorinated gases, SF_6/O_2 [7,8,9] and CF_4/O_2 [8], known to etch W films either have not been investigated in the low-pressure RIE mode necessary for fine-line patterning or have not exhibited the necessary selectivity.

II. Experimental Conditions

W films were deposited at room temperature by DC magnetron sputtering from a 99.97% purity W target in an Ar plasma .A W sputtering rate of 10nm/min was generally used. After deposition , W films were treated by RTA (HeatPulse 120/T) using a broad band, high intensity tungsten lamp in Ar ambient atmosphere from 500C to 1100C for a duration of 10 to 90 seconds .The purity of the argon gas used for both deposition and annealing was higher than 99.999%. The sheet resistance of W film was measured before and after RTA using a four-point probe system . X-ray spectroscopy was used to investigate the crystallinity of the W thin films achieved by RTA.

The etching experiments were carried out in a parallel plate reactor (Plasma Therm PK1241 , 13.65MHz) equipped with a computer-controlled grating monochromator for measuring optical emission within the plasma. The fluorinated gases used in our investigation were CF_4 (99.9% purity), SF_6 (99.997%) and CHF_3 (>98%) mixed with O_2 (99.99%). Emission spectra from the plasma, in the wavelength range

between 200 to 800 nm, were monitored during etching through a quartz window located on the sidewall of the chamber. To provide a suitable basis of comparison, the RF power, pressure and gas flow rate were kept constant at 200W(0.42W/cm^2), 20mTorr and 20sccm, respectively. To determine the etch rate in various gas plasmas, aluminum was used as a thin film mask since it is suitable for both low- and high-percentage oxygen mixture in the plasma. The Al mask was subsequently removed by wet etching for step height determination by a profilometer (Dektak). The anisotropy of the etching process was investigated by scanning electron microscopy (Nanometrics Cwickscan II).

III. Results

W films of 300 to 500nm were deposited on Si and SiO_2 for annealing and etching experiments. RTA was found to be very effective at reducing the resistivity of the W films. As shown in Fig.1 for a annealing temperature of 1100 C, the resistivity decreased a factor of five during the first 10 sec after which it decreased more gradually for additional annealing time. This behaviour was observed in all isothermal anneals at temperatures from 500 C to 1100 C. Therefore, the RTA annealing conditions of 30sec,1100C, Ar ambient were chosen to prepare samples for the etching study. Isochronal anneals, shown in Fig.2 for a 90sec RTA duration, indicate an Arrhenius-type behaviour for the W thin film conductivity with an activation energy of 0.46 eV.

X-ray diffraction patterns of W thin films deposited on oxidized Si <100> wafers were taken for each annealing temperature and compared to the as-deposited films. It was found that with increasing temperature the W films became strongly <110> oriented [10].

For reactive ion etching, the etch rates were determined as a function of oxygen percentage in CF_4, SF_6 and CHF_3. In Fig.3a, the CF_4 etch rate for annealed and unannealed W samples, along with the rates for Si and SiO_2, is shown as a function of oxygen percentage (from 0% to 90%) at a power of 200W, a pressure of 20mTorr and a total flow rate of 20sccm. In Fig.3b are shown the corresponding DC self-bias and the relative intensity of fluorine [F] and oxygen [O] emission at 703.7 and 780nm, respectively. As reported by Mogab, Adams and Flamm [11] and various other workers, the addition of relatively small amounts of oxygen to CF_4 increases the Si etch rate as the oxygen consumes fluorocarbon radicals and liberates additional fluorine species. Beyond a certain concentration, however, increasing amounts of oxygen have the opposite effect, as the oxygen-rich mixture dilutes the CF_4 gas and also lowers the energy of electrons in the plasma which in turn reduces the electron-induced dissociation rate of CF_4. Another effect important at high O_2 concentrations is the competition for active etching sites on the surface between [F] and chemisorbed O atoms [11] . In general, however, the variation of the [F] intensity with O_2 % is roughly mirrored in the Si etch rate.

The annealed W etch rate behaviour with O_2 % appears to

also follow the [F] intensity, but the relationship is much less pronounced. However, all three parameters (Si and W etch rates,[F intensity) exhibit a peak value for a 20% oxygen mixture. This is in contrast to the offset between O_2 concentrations for maximum [F] intensity and peak etch rate reported for CF_4/O_2 plasma (vs. RIE mode in this work) etching of Si [11] and W [8] at high pressure (200, 350mT). As mentioned above, this offset is generally attributed to a partial masking of the surface by chemisorbed oxygen. A possible explanation for the different behaviour observed in our RIE-mode experiments is the presence of a fairly high self-bias voltage (>400V). This results in more energetic ions than in the plasma etching mode which are probably more effective at removing chemisorbed oxygen from the surface. This, in turn, liberates additional sites for the etching process and enhances the etch rate.

In general, for all the gases investigated the unannealed W films display an etch rate dependence on the oxygen concentration which exhibits one region of higher etch rate than that of annealed films. This is most likely due to the "densification" of the films as they become more crystalline upon annealing. A similar effect has been observed in the plasma etching of other refractory materials, for example $MoSi_2$ films etched in CF_4/O_2 [12]. For unannealed W etched in CF_4/O_2, the etch rate peaks with a value of 110 nm/min for a richer oxygen mixture than the annealed films, 50% vs. 20% . For the CF_4/O_2 RIE process, the (anneal)W:Si etch rate

selectivity is considerably less than unity for O_2 mixtures of less than 50%. For O_2 mixtures greater than 50%, the selectivity does increase above unity (for example, 2:1 at 80% O_2), but under the restriction of rather low etch rates (40 and 20 nm/min for W and Si, respectively, at 80% O_2).

The etch rates of W, Si and SiO_2 in SF_6/O_2 mixtures are shown in Fig.4a. The corresponding DC self-bias and the relative intensity of fluorine and oxygen in the plasma are shown in Fig.4b. The greater abundance of fluorine species in SF_6/O_2 mixtures results in a much greater Si etch rate. The maximum Si etch rate of 2.2um/min occurs at 10% O_2 concentration, even though the peak [F] emission intensity takes place at 30% O_2. This result is very similar to that reported by Pinto et. al. [13] for Si RIE at 10mT, 50sccm and $0.4W/cm^2$, namely a peak etch rate of 1.3um/min at 10% O_2. The offset between the maximum Si etch rate and the peak [F] intensity in SF_6 etching versus its absence in CF_4 plasma can be explained by the considerably lower(approx. a factor of 2) DC bias found in the former case at small oxygen percentages, which is probably less effective in removing chemisorbed oxygen from the surface. Indeed, Pinto et. al. report that as the power density (and consequently the DC bias) is lowered the resulting etch rate is not only lowered, but the peak in the etch rate vs. O_2 shifts to lower oxygen concentrations.

The reactive ion etching characteristics of annealed and unannealed tungsten films in the SF_6/O_2 plasma are seen from Fig. 4a to vary significantly. The unannealed W films have an etch rate vs. O_2 dependence that is similar to the Si case. A

pronounced etch rate peak of 580nm/min is obtained at 5% O_2 concentration. For richer O_2 mixtures, the etch rate drops sharply. The maximum-to-minimum etch rate ratio for W(unannealed) over the range of oxygen mixtures is almost 30. The annealed W films exhibit a markedly different behaviour for O_2 concentrations lower than 30%. In this case the maximum etch rate of 180 nm/min occurs for the pure SF_6 gas and the max-to-min etch rate ratio is only 6. However, it is interesting to note that both types of W films had roughly the same characteristics for O_2 concentrations of 30% and higher.

The reactive ion etching rates using CHF_3 and O_2 mixtures are shown in Fig. 5a and the corresponding DC bias, [F], [O] and [H] emission (at 780 nm) are shown in Fig. 5b. In the pure CHF_3 plasma, the fluorine species concentration is diluted because of the high hydrogen concentration and by direct reaction with H forming H molecules [14]. This decrease in [F] reduces the Si etch rate considerably, while the presence of HF increases the SiO_2 etch rate [15]. In Fig. 5b, we show that addition of large amounts of O_2 does result in a slight increase in the [F], with a peak at approximately 65% O_2. The Si etch rate peaks at 50% O_2 with a value of 55 nm/min. By comparison, the maximum Si etch rate in SF_6 is 2.2 um/min or 40 times larger.

The W film etch rate in CHF_3/O_2 plasma is also strongly affected by the lower [F] concentration, especially at low O_2 % levels, where the [H] is quite high. However, in the vicinity of the [F] peak at 60 - 70% O_2 mixtures, the

W etch rate increases substantially . The highest (unannealed)W etch rate was 950A/min at 70%O_2, and its ratio to Si and SiO_2 etch rates are 2.4 and 2.1 , respectively. The corresponding etch rate ratios for annealed W are 1.6 and 1.8 . For reverse selectivity, the optimum etching takes place in pure CHF_3, where the following etch rate ratios are obtained: annealed W to Si and SiO_2 of 1:3.2 and 1:4.6 and unannealed W to Si and SiO_2 of 1:7.7 and 1:5.3, respectively.

The optimum selectivities of reactive ion etching are summarized in Table I. A W:Si etch rate ratio greater than unity was shown for the first time to be achievable using CHF_3/70%O_2, where a selectivity of 1.6:1 and 2.4:1 were measured for annealed and as-deposited W films. The highest reverse W:Si selectivity of 1:11.6 was obtained for annealed W films with SF_6/5%O_2. For W:SiO_2 selectivity , the optimum values are obtained at SF_6/5%O_2, while the optimum reverse selectivity is found in pure CHF_3 plasma.

The edge profile of W film etched by reactive ion etching was preliminarily investigated for conditions observed to produce optimum W-to-Si and W-to-SiO_2 selectivity. Unannealed W films, 0.7 um thick,were etched in CHF_3/70%O_2 and SF_6/5%O_2 at 20mTorr, 200W, and 20sccm. A 4um W line on Si patterned with CHF_3/70% O_2 is shown in Fig. 6 with the Al mask layer still in place. Very little undercutting of the W or etching of the Si substrate is observed. As can be seen from the SEM microphotographs in Figs. 7 and 8, the vertical-to-lateral etch ratio of the W film is 3.5:1 in CHF_3/70%O_2 and 2:1 in SF_6/5%O_2.

IV. Discussion

The resistivity of thin W films has been reported [1] to vary substantially depending on the deposition technique, with results generally a factor of 2 to 3 higher than the bulk value of 5.6 micro ohm-cm. Also, the resistivity has been shown [16,17] to be a function of film thickness, sometimes requiring a thickness of 1um or more to achieve the lowest value. Tungsten films deposited by DC sputtering and subjected to conventional furnace heat treatment (passivation at 1000 C and annealing at 450 C), have been reported [18] to have a resistivity of around 20 micro ohm-cm for a film thickness of 300nm. Our results using rapid thermal annealing of DC-sputtered films of the same thickness compare favorably with conventional processing, yielding a resistivity of around 16 micro ohm-cm for a 90 sec, 1100 C anneal.

The study of plasma-assisted etching of thin films suffers from an "embarrassment of riches" in the many parameters which can be varied (cf. main plasma gas, dilutant, sample placement vis-a-vis ion bombardment, power, pressure, flow rate, etc.). In this work, we have therefore confined ourselves to fluorinated gases diluted with oxygen and operating in the RIE mode at a fixed pressure, flow rate and power. As discussed in the previous section, a very strong, but complex, relationship is evident between the amount of oxygen in each of the three fluorinated gases (CF_4, SF_6 and CHF_3) investigated, the fluorine concentration and the resulting W and Si etch rates. This complex relationship is highlighted in

the case of W in Fig. 9 where the normalized W etch rate and fluorine intensity are plotted as a function of oxygen percentage for each gas. The peak W etch rate occurs at oxygen concentrations ranging from zero to 70%. The fluorine maximum intensity coincides with the peak in etch rate for some but not all cases. In Table II we compare the effect of oxygen on our results with those of related work from the literature by indicating the O_2 percentage in the gas mixture at which the [F] intensity, and the Si or W etch rate reach their maximum value. For comparison purposes, we have also included corresponding plasma etching results from the literature.

For the case of CF_4/O_2 mixtures, both our results with W RIE and others for W and Si PE [8,14] indicate a [F] peak at 20-23% O_2 mixtures. However, under RIE conditions the W and Si etch rate maximum are coincident with the [F] peak, whereas the PE results published indicate a shift in the maximum etch rate to leaner oxygen mixtures. In the case of SF_6/O_2 etching, both W PE and RIE of W and Si exhibit this shift. Finally, in the case of CHF_3/O_2, a shift is observed for Si RIE but not for W etching.

To understand the role of fluorine radicals in the reactive ion etching process we plot in Fig.10 the etch rates of Si, SiO_2, and as-deposited and annealed W as a function of measured fluorine emission intensity obtained at various oxygen mixtures. As can be see all cases, except for SiO_2, exhibit a substantial hysteresis effect where for the same [F] intensity

two widely different etch rates can result. This effect has been previously observed in the plasma etching of Si in CF_4/O_2 [11] and SF_6/O_2 [19] mixtures. As mentioned in Sec. III , this effect has been attributed [11,19] to the competition between fluorine and oxygen atoms for chemisorption sites on the Si surface. Thus, the availability of increasing amounts of [F] is not always the rate limiting step, if it is accompanied by an equal or greater increase in oxygen concentration. In the case of W RIE, our data also exhibits hysteresis, indicating that a similar mechanism is at work. The situation is quite different for SiO_2, since oxygen forms an intrinsic part of the material to be etched. Consequently, no hysteresis effect is observed, but rather a generally increasing trend in etch rate with [F], with a similarly large scatter in the data as reported by Mogab et. al. [11] for SiO_2 plasma etching in CF_4/O_2 mixtures.

To further elucidate the competing roles of fluorine and oxygen we have plotted in Fig. 11 the normalized Si and W etch rates as a function of the ratio of [F] to [O] emission intensity in all three gas mixtures. The [O] emission level at each point is taken with respect to the base line level found in the "pure" gas plasma. A number of points can be made about the information contained in Fig.11 First, the hysteresis effect in the etch rate is removed by taking both [F] and [O] into account. Second, the etch rate trends for Si and W are the same in each gas plasma. Third, the pattern is substantively different for RIE in CF_4/O_2 and SF_6/O_2 from RIE in CHF_3/O_2. For the former, the etch rate increases with [F]/[O] ratio until

it gradually reaches saturation. In the latter case, the pattern is clearly non-monotonic with a peak in etch rate present at a [F]/[O] ratio of 1.44 for Si and approximately 1 for W. The decrease in etch rate after the peak takes place in mixtures with increasing levels of hydrogen. This clearly points out the inhibiting role of hydrogen in the W and SiO_2 etch rate.

V. Summary and Conclusions

In summary, high quality W thin films were successfully prepared by sputtering and RTA techniques. The reactive ion etching of annealed and as-deposited W films, along with Si and SiO_2, was inve igated in CF_4/O_2, SF_6/O_2 and CHF_3/O_2 plasmas. A W:Si etch rate ratio greater than unity was for the first time obtained with oxygen-rich CHF_3 mixtures. The competing role of fluorine and oxygen in the etching process was investigated. Hydrogen was found to be necessary to obtaining a high W:Si selectivity, by depressing the Si etch rate.

Acknowledgment

The Authors would like to acknowledge partial support for this work from the Office of Naval Research, under ONR contract No.Nooo14-81-K-0605.

References

[1] T.P Chow and A.J. Steckl, "A Critique of Refractory Gate Applications for MOS VLSI, Ch.2 in VLSI Electronics, Vol. 9, N. Einspruch, ed., Academic Press, NY (1985)

[2] Robert S. Blewer, "Progress in LPCVD Tungsten for Advanced Microelectronics Applications", Solid State Technology, p.117, Nov (1986)

[3] E.K. Broadbent and W.T. Stacy,"Selective Tungsten Progressing by low Pressure CVD", Solid State Technology, Vol.2, no.12, p.51, Dec(1985)

[4] J.M. Shaw and J.A. Amick,"Vapor-deposited tungsten as metallization and interconnection materials for silicon devices",RCA Rev., Vol.31, pp.306(1970)

[5] K.Y. Tsao and H.H. Busta, " Low Pressure Vapor Deposition of Tungsten on Polycrystalline and Single-Crystal Silicon via the Silicon Reduction ", J. Electrochem. Soc., Vol.131, 2702(1982)

[6] A. Gat, J.F. Gibbons, T.J. Magee, J. Peng, V.R. Deline, P. Williams, and C.A. Evans, Jr, "Physical and Electrical Properties of Laser-Anneal Ion Implanted Silicon", Appl. Phys. Lett. 32, 276(1978)

[7] J.N. Randall and J.C. Wolfe, "High-resolution pattern definition in tungsten", Appl. Phys. Lett., Vol.39, 742(1981)

[8] C.C. Tang and D.W. Hess, "Tungsten Etching in CF_4 and SF_6 Discharges", J. Electrochem. Soc., Vol. 131, 115, Jan(1984)

[9] A. Picard and G. Turban, "Plasma Etching of Refractory Metals (W,Mo,Ta) and Silicon in SF_6 and SF_6-O_2. An Analysis of Reaction Products", Plasma Chemistry and Plasma Processing, Vol.5, no.4, 333(1985)

[10] W.S. Pan and A.J.Steckl, to be published.

[11] C.J. Mogab, A.C. Adams and D.L. Flamm, "Plasma Etching of Si and SiO_2-The Effect of Oxygen Addition to CF_4 Plasma", J. Appl. Phys., Vol.49,3796(1978)

[12] T.P. Chow and A.J. Steckl, "Plasma Etching Characteristics of Sputtered MoSi2 Films", Appl. Phys. Lett., Vol. 37,466 (1980).

[13] R. Pinto, K.V. Ramanathan and R.S. Babu, "Reactive Ion Etching in SF_6 Gas Mixtures", Vol. 134, 165(1987).

[14] R.A.H. Heinecke, "Control of Relative Etch Rates of SiO_2 and Si Plasma Etching", Sol. State Electron., Vol.18, 1146 (1975).

[15] H.W. Lehmann and R.Widmer, "Profile Control by Reactive Sputter Etching", J. Vac. Sci. Technol., Vol.15, 319(1978).

[16] M.L. Green and R.L. Levy, "Structure of Selective Low Pressure Chemically Vapor Deposited Films fo Tungsten", J. Electrochem. Soc., Vol.132, 1243 (1985)

[17] A.J. Learn and D.W. Foster,"Resitivity, Grain size and Impurity in CVD Tungsten Films", J. Appl. Phys., Vol.58, 2001(1985).

[18] P.L. Shah, "Refractory Gate Processes for VLSI Applications", IEEE Trans. Electron Devices, Vol. ED-26, 631(1979)

[19] R. d'Agostino and D.L. Flamm, "Plasma Etching of Si and SiO_2 in SF_6-O_2 Mixtures", J. Appl. Phys. Vol.52, 163(1981)

List of Tables and Figures

CF_4, SF_6 and CHF_3 with O_2 plasma under RIE mode.

Fig.10(d) Etch rate of SiO_2 versus [F] intensity in CF_4, SF_6 and CHF_3 with O_2 plasma under RIE mode.

Fig.11(a) The normalized etch rate of W(anneal) and Si versus $[F]/[O]_\Delta$ (which was normalized to background value) ratio in CF_4/O_2 plasma.

Fig.11(b) The normalized etch rate of W(anneal) and Si versus $[F]/[O]_\Delta$ ratio in CHF_3/O_2 plasma.

Fig.11(c) The normalized etch rate of W(anneal) and Si versus $[F]/[O]_\Delta$ ratio in SF_6/O_2 plasma.

Table I. Maximum Selectivities Observed for W:Si and W:SiO_2

Selectivity		$CHF_3/7\%O_2$	CHF_3	$SF_6/5\%O_2$	$SF_6/30\%O_2$
W_a*	: Si	1.6:1	1:3.2	1:11.6	1:10
W_a	: SiO_2	1.8:1	1:4.6	3:1	2.5:1
W_{una}**	: Si	2.4:1	1:5.4	1:3	1:10
W_{una}	: SiO_2	2.1:1	1:7.6	11.6:1	2.3:1

RIE Etching Conditions : 200W, 20sccm, 20mTorr

* W_a : annealed W film

** W_{una} : unannealed W film

Table II. Comparison of Results for Fluorine/Oxygen-Based Plasma-Assisted Etching of Si and W

	CF_4/O_2		SF_6/O_2		CHF_3/O_2
Mode , Pressure & Power Density	[a]: PE 350mT 0.16W/cm^2 [b]: PE 200mT 0.2W/cm^2	[c]: RIE 20mT 0.4W/cm^2	[b]: PE 200mT 0.2W/cm^2 [d]: PE 1T ~1.6W/cm^2	[c]: RIE 20mT 0.4W/cm^2 [e]: RIE 10mT 0.4W/cm^2 [f]: RIE 10mT	[c]: RIE 20mT 0.4W/cm^2
[F] peak	23%[a] 20%[b]	20%[c]	30%[b] 30%[d]	30%[c]	65%[c]
Si E.R.* peak	12%[a]	20%[c]	30%[d]	10%[c] 10%[e]	50%[c]
W E.R.* peak	10%[b]	20%[c] (50%)	0%[b]	0%[c] (5%) 0%[f]	65%[c] (70%)

[a]: Mogab et.al.[11]
[b]: Tang & Hess[8] {W as-deposited at 350 C}
[c]: Pan & Steckl[this work] {W RTannealed at 1100 C, (W as-deposited & 25 C)}
[d]: d'Agostino and Flamm [19]
[e]: Pinto et.al.[13]
[f]: Randall & Wolfe[7] {W as-deposited at 25 C}

* E.R. peak : Maximum Etch Rate

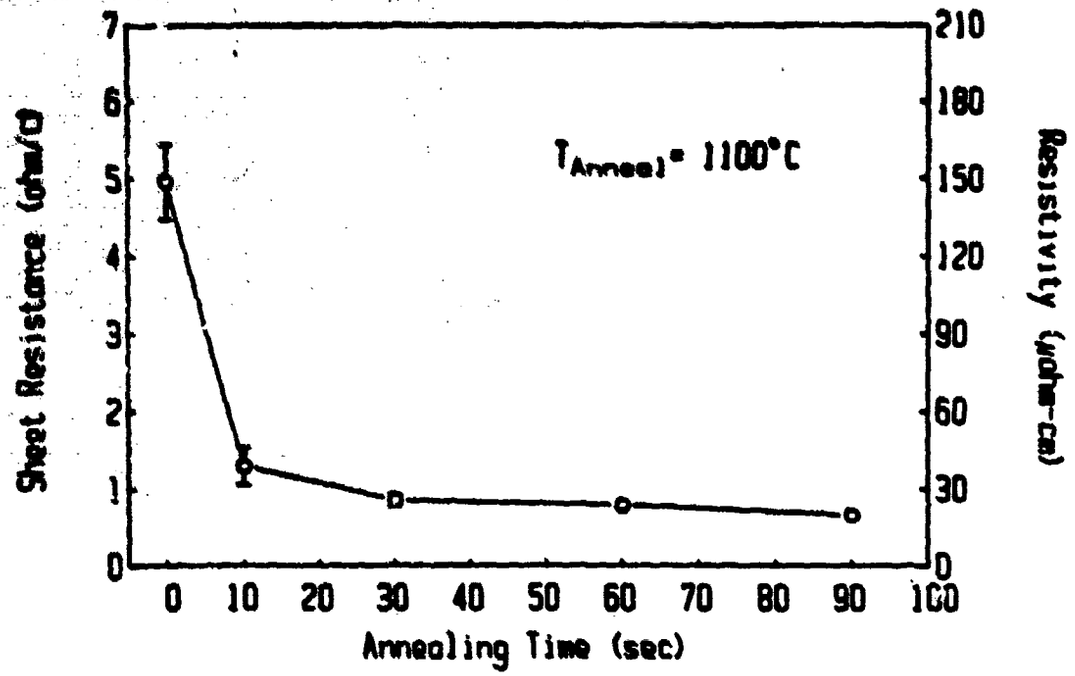
Sheet Resistance (ohm/□)
Resistivity (μohm-cm)
T_{Anneal} = 1100°C
Annealing Time (sec)
0
1
2
3
4
5
6
7
30
60
90
120
150
180
210
0
10
20
30
40
50
60
70
80
90
100

Fig. 1

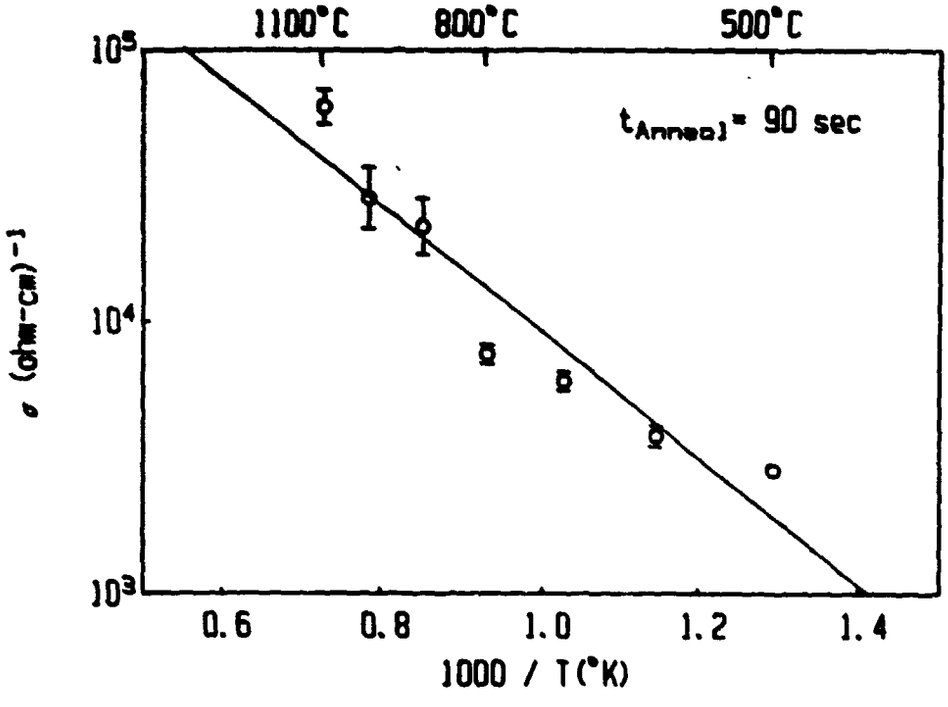
1100°C
800°C
500°C
t_{Anneal} = 90 sec
σ (ohm-cm)$^{-1}$
10^5
10^4
10^3
0.6
0.8
1.0
1.2
1.4
1000 / T(°K)

Fig. 2

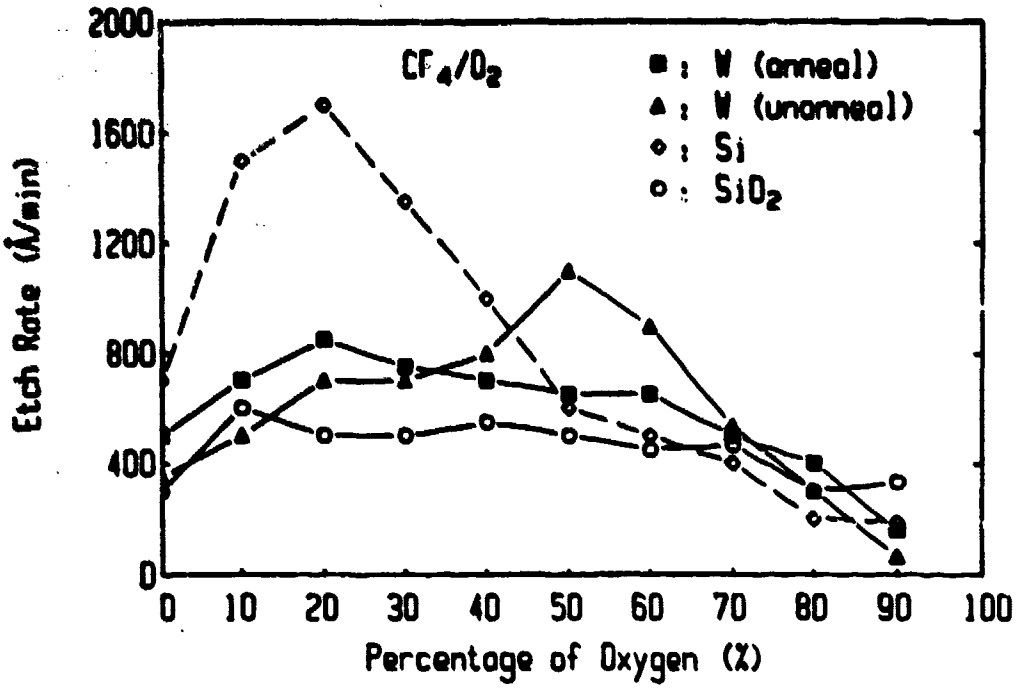
CF_4/O_2
■ : W (anneal)
▲ : W (unanneal)
◇ : Si
○ : SiO_2
Etch Rate (Å/min)
2000
1600
1200
800
400
0
0 10 20 30 40 50 60 70 80 90 100
Percentage of Oxygen (%)

Fig. 3a

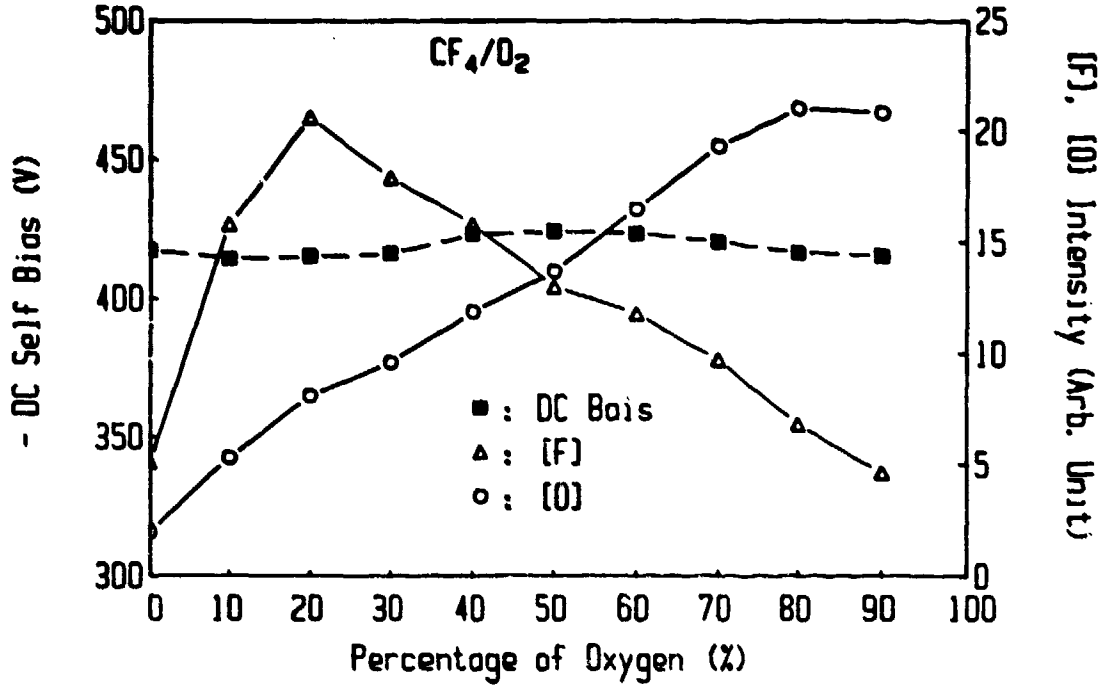
CF_4/O_2
■ : DC Bais
▲ : [F]
○ : [O]
- DC Self Bias (V)
500
450
400
350
300
25
20
15
10
5
0
[F], [O] Intensity (Arb. Unit)
0 10 20 30 40 50 60 70 80 90 100
Percentage of Oxygen (%)

Fig. 3b

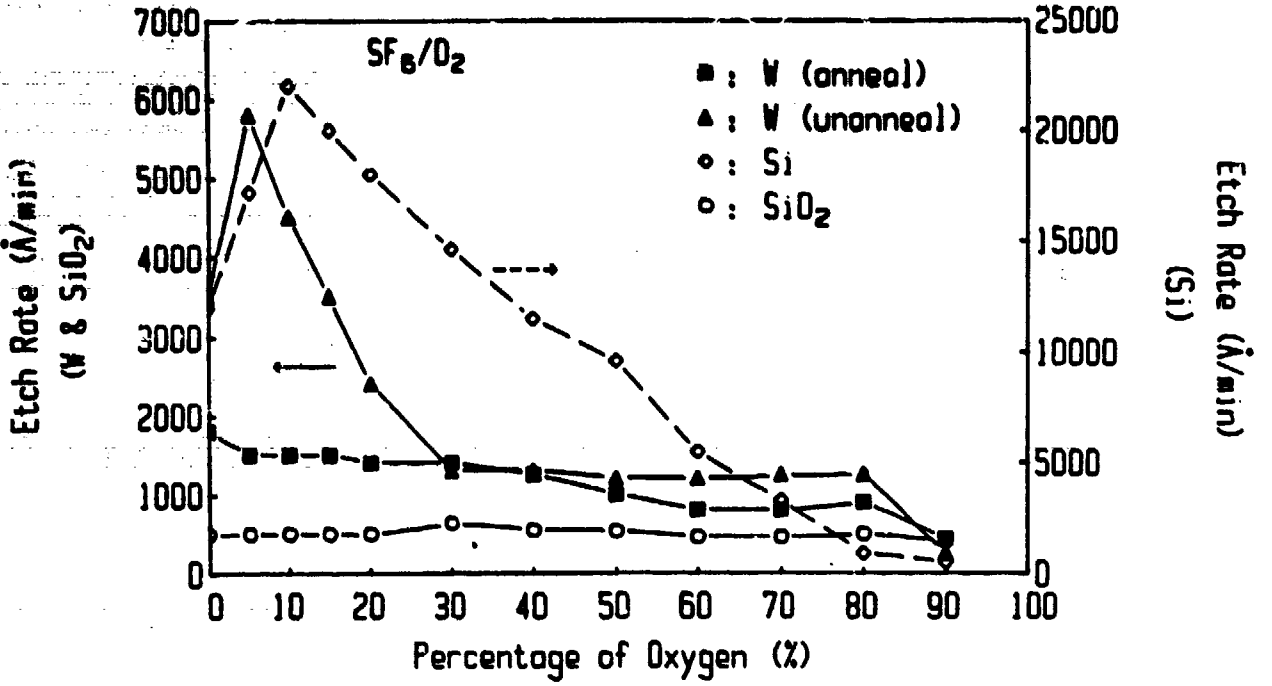
SF_6/O_2
■ : W (anneal)
▲ : W (unanneal)
○ : Si
○ : SiO_2
Etch Rate (Å/min) (W & SiO_2)
Etch Rate (Å/min) (Si)
Percentage of Oxygen (%)

Fig. 4a

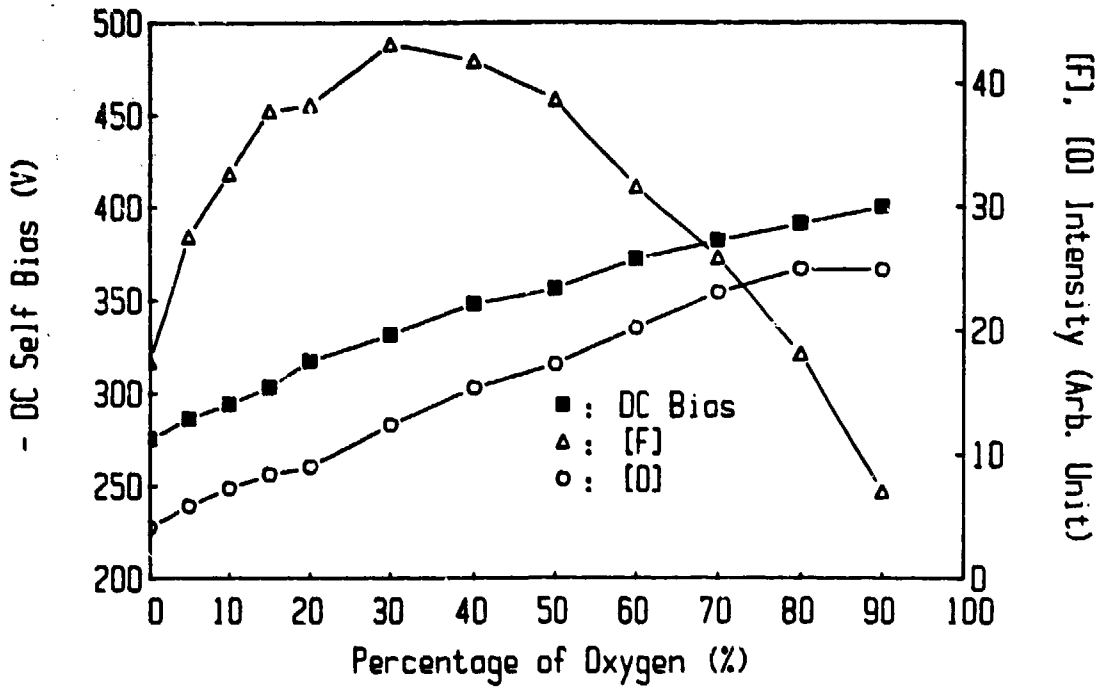
■ : DC Bios
△ : [F]
○ : [O]
- DC Self Bios (V)
[F], [O] Intensity (Arb. Unit)
Percentage of Oxygen (%)

Fig. 4b

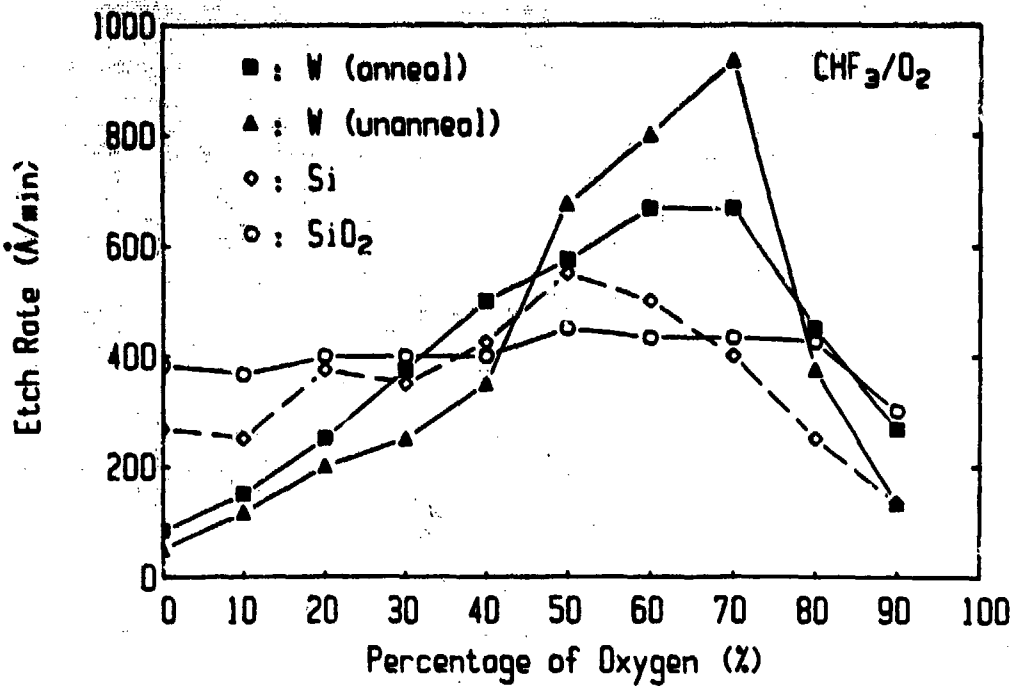
■ : W (anneal)
▲ : W (unanneal)
◇ : Si
○ : SiO_2
CHF_3/O_2
Etch Rate (Å/min)
Percentage of Oxygen (%)

Fig. 5a

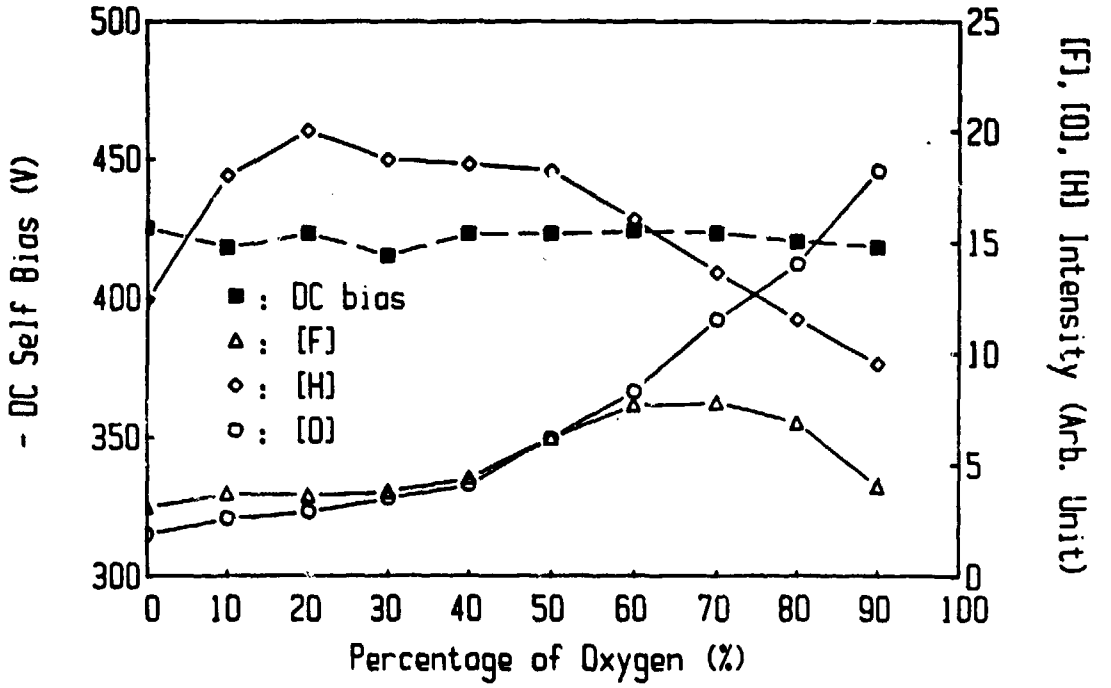
■ : DC bias
△ : [F]
◇ : [H]
○ : [O]
- DC Self Bias (V)
[F], [O], [H] Intensity (Arb. Unit)
Percentage of Oxygen (%)

Fig. 5b

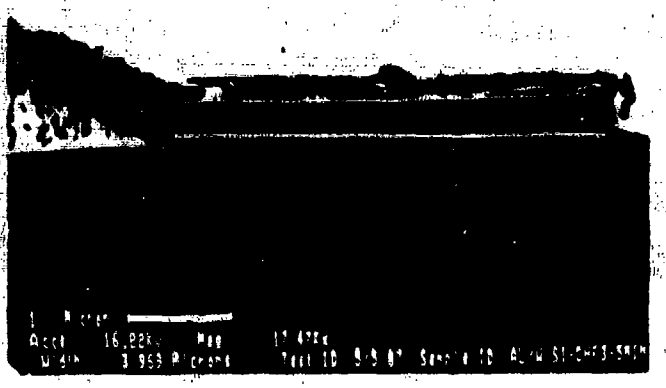

Fig. 6

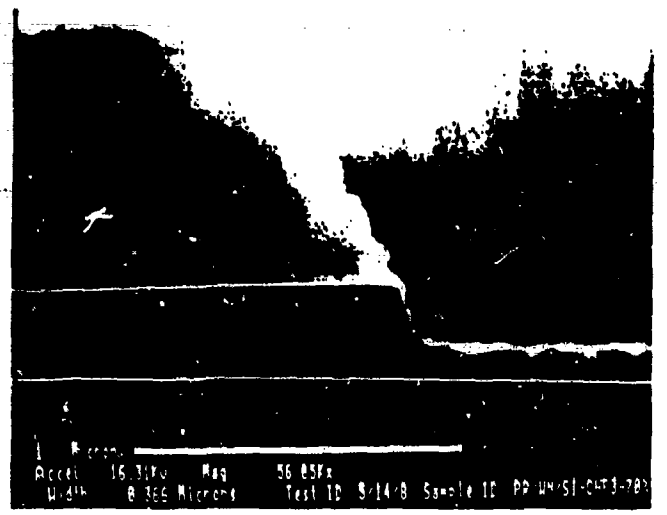

Fig. 7

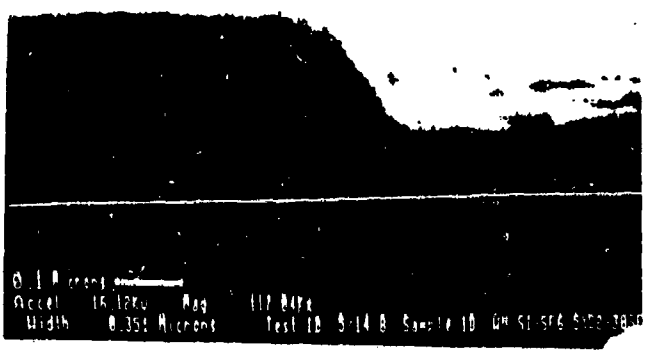

Fig. 8

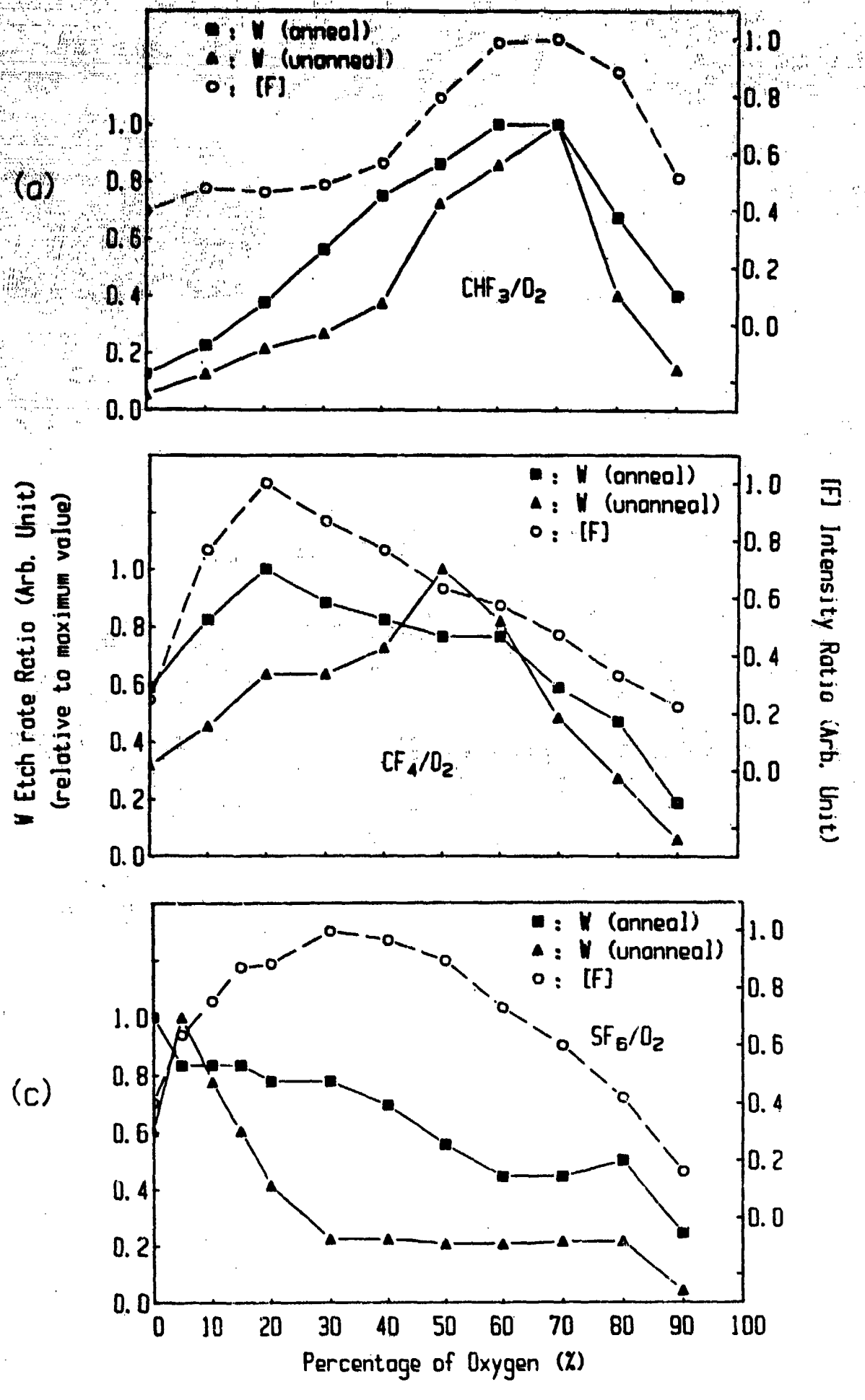
■ : W (anneal)
▲ : W (unanneal)
○ : [F]
(a)
CHF_3/O_2
(b)
CF_4/O_2
(c)
SF_6/O_2
W Etch rate Ratio (Arb. Unit)
(relative to maximum value)
[F] Intensity Ratio (Arb. Unit)
0.0
0.2
0.4
0.6
0.8
1.0
0
10
20
30
40
50
60
70
80
90
100
Percentage of Oxygen (%)

Fig. 9a, b, c

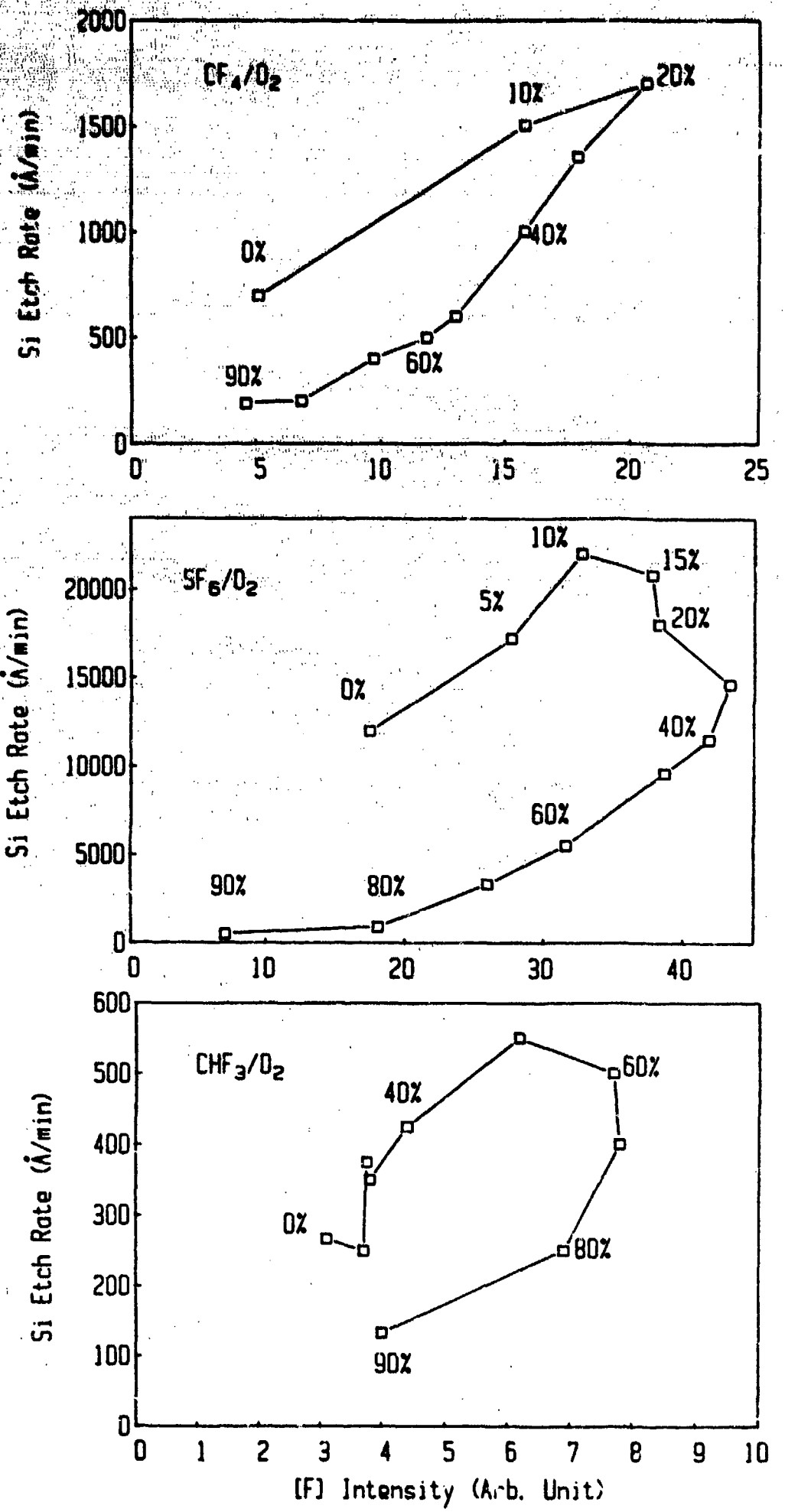
CF_4/O_2
0%
10%
20%
40%
60%
90%
Si Etch Rate (Å/min)
2000
1500
1000
500
0
0
5
10
15
20
25
SF_6/O_2
0%
5%
10%
15%
20%
40%
60%
80%
90%
Si Etch Rate (Å/min)
20000
15000
10000
5000
0
0
10
20
30
40
CHF_3/O_2
0%
40%
60%
80%
90%
Si Etch Rate (Å/min)
600
500
400
300
200
100
0
0
1
2
3
4
5
6
7
8
9
10
[F] Intensity (Arb. Unit)

Fig. 10a

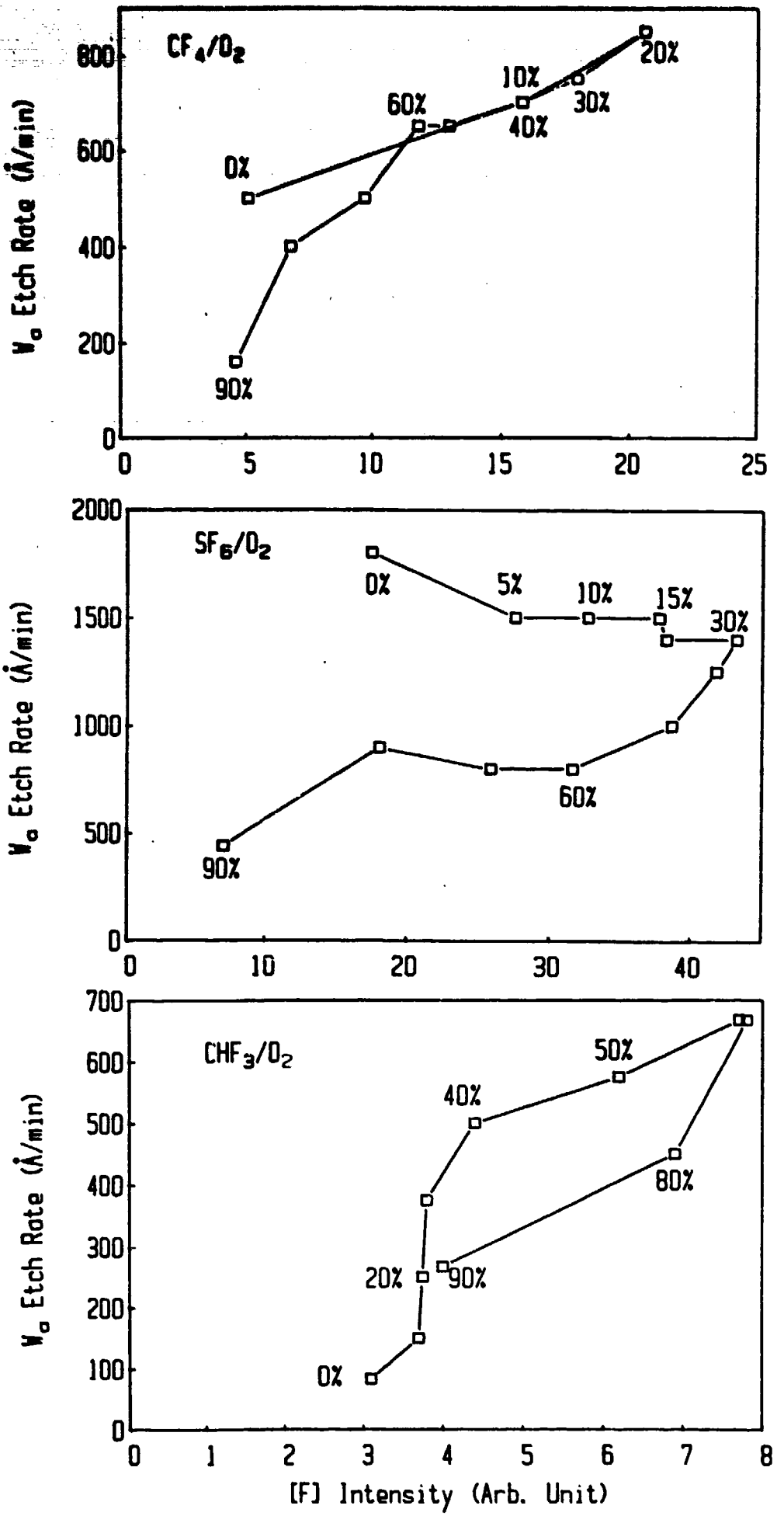
CF_4/O_2
0%
10%
20%
30%
40%
60%
90%
V_o Etch Rate (Å/min)
SF_6/O_2
0%
5%
10%
15%
30%
60%
90%
V_o Etch Rate (Å/min)
CHF_3/O_2
0%
20%
40%
50%
80%
90%
V_o Etch Rate (Å/min)
[F] Intensity (Arb. Unit)

Fig. 10b

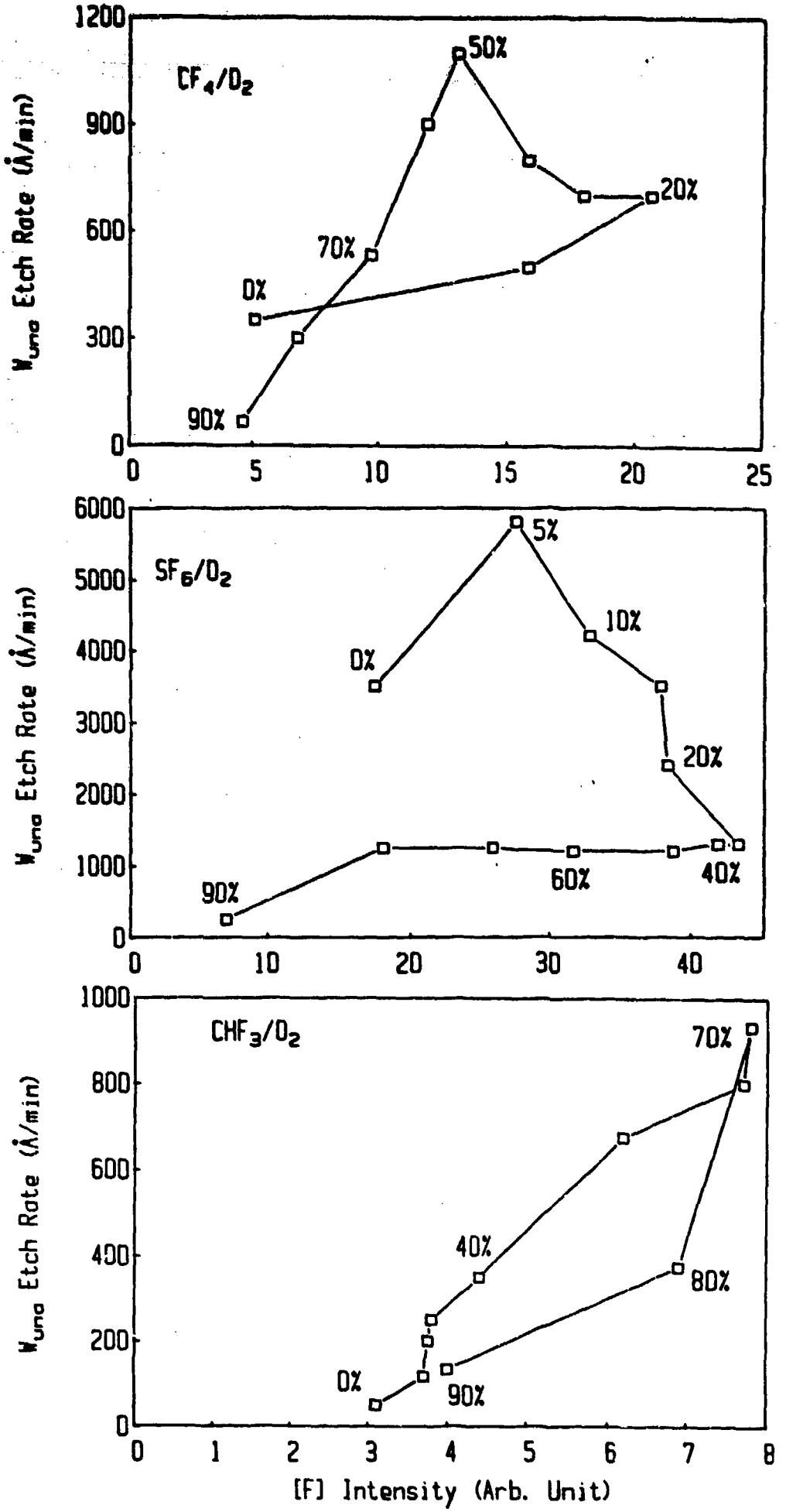
CF_4/O_2
W_{uno} Etch Rate (Å/min)
1200
900
600
300
0
50%
70%
20%
0%
90%
0
5
10
15
20
25
SF_6/O_2
W_{uno} Etch Rate (Å/min)
6000
5000
4000
3000
2000
1000
0
5%
10%
0%
20%
90%
60%
40%
0
10
20
30
40
CHF_3/O_2
W_{uno} Etch Rate (Å/min)
1000
800
600
400
200
0
70%
40%
80%
0%
90%
0
1
2
3
4
5
6
7
8
[F] Intensity (Arb. Unit)

Fig. 10c

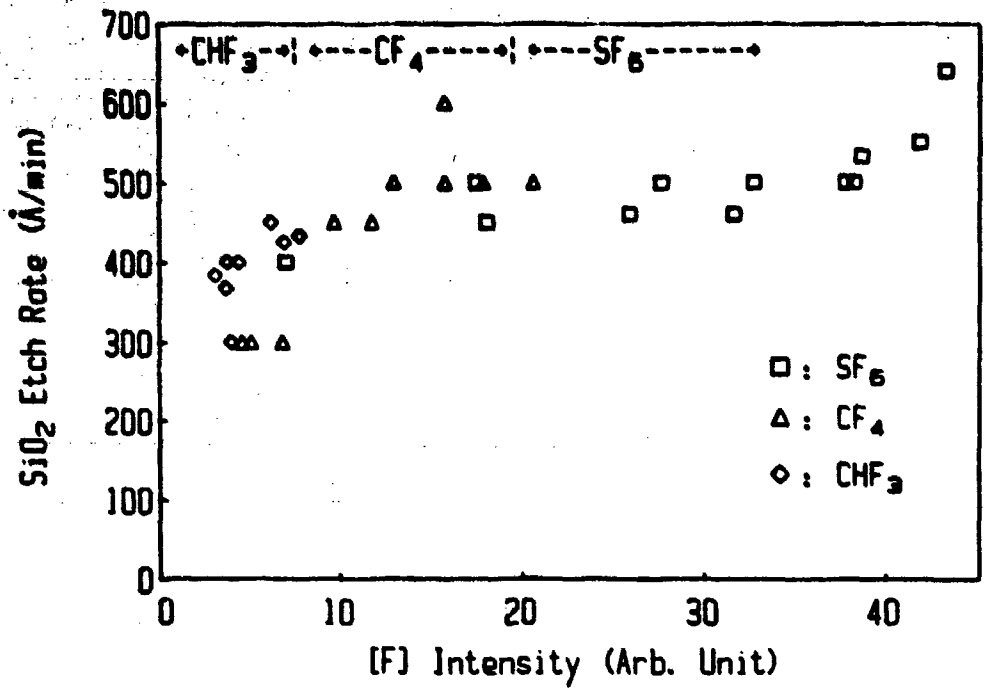

Fig. 10d

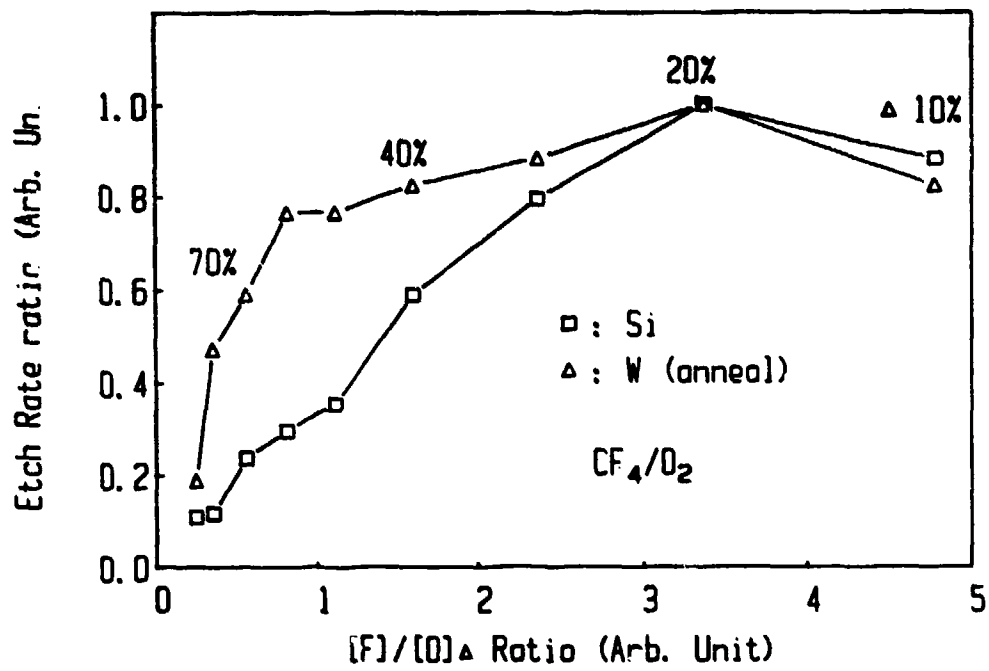

Fig. 11a

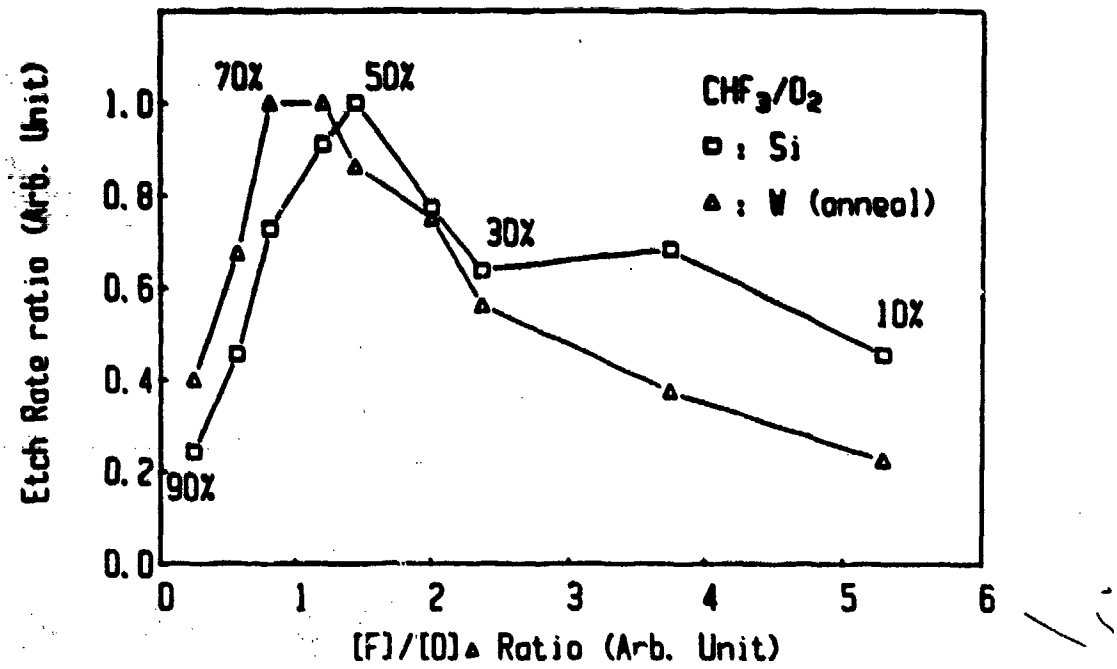

Fig. 11b

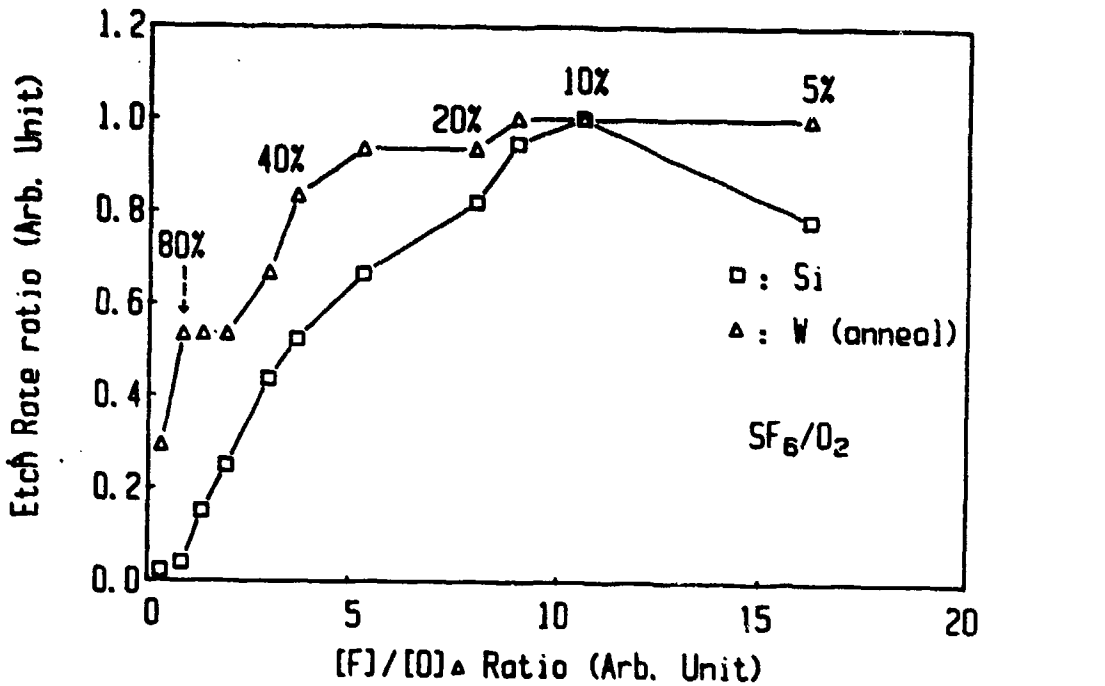

Fig. 11c